Title of Initiative

Theory of Quantum Effect on Degenerate Dense Plasma

Authors of Initiative:
Tadashi Ogitsu (PI), Alfredo Correa (Co-I), Xavier Andrade (Co-I)
Email of corresponding author:
ogitsu1@llnl.gov
Topical area(s): HEDP, and/or Discovery Plasma.

Goals of Initiative

Our primary goal is to obtain accurate and detailed information about electron-ion relaxation processes of strongly driven systems that include, but are not limited to, degenerate dense plasma (DDP) systems created by strong perturbations. These systems include interactions from short pulse lasers or radiation damage on materials and biological systems through (1) developing ab-initio based adjustable-parameter-free multi-scale computational methods for modeling highly electron-ion nonequilibrium systems, (2) validating the simulation results through collaborative research with experimentalists in the community, and (3) sharing the outcome with the scientific community and industry via software distribution, publication and an online database.

The TRLs of the methods discussed in this white paper are mostly deployable, however, their accuracies are largely unknown. Therefore, quantifying the uncertainty and identifying the origin of errors will be the initial goal of our initiative, which will then be used to decide the next direction to optimize research and best achieve critical mission advancements for DOE.

Description of the Initiative

Understanding the quantum mechanical properties of DDP is a growing research area due to recent advances in fusion science, laser science and planetary physics[1]. The DDP regime lies between condensed matter and plasmas, where it is defined by temperatures of 10^4-10^5 K (1–10 eV) and near solid densities. In addition to the challenges in understanding a system that doesn't conform to the traditional plasma and/or condensed matter physics (thermal energy is comparable to the Fermi energy and the ion-ion coupling parameter is of the order of unity), experimental DDP states are obtained in the laboratory by transient methods, implying that the system is a fundamental aspect under non-equilibrium conditions. Due to the diverse coupling of light with the different components of the material, the first obvious non-equilibrium aspect is the energy excitation at which electrons and ions are found after laser excitation. In turns, this triggers non-equilibrium phase transitions and material responses under idealized conditions as well as a complicated interplay of interactions in their path to equilibrium.

While heat-diffusion-hydrodynamic and molecular dynamics are the tools of choice for modeling matter, advanced multi-physics approaches are necessary to tackle these non-equilibrium problems. We propose using a combination of techniques that separately, can take into account several conditions. This includes such examples as sample expansion or pressure increase, electron ejection[2], phonon-softening[3]/hardening[4, 5], changes in specific heat and electron-phonon

coupling[6], two-temperature modeling[7] (diffusive in the inhomogeneous case[8]), ab initio and/or empirical molecular dynamics.

To this end, we propose to develop a multi-scale method consisting of four thrust areas:

Thrust 1. Development of ab-initio derived thermophysical parameters [specific heat (C), electron-ion coupling (G), thermal conductivity (K)] under electron-ion non-equilibrium DDP conditions.

Thrust 2. Development of a real-time time-dependent-density functional theory (RT-TDDFT), which will provide us insights into the nature of coupled electron-ion dynamics.

Thrust 3. Development of a one dimensional Two-Temperature-Model (TTM) with fully electron-ion dependent thermophysical parameters that are provided by **(Thrust 1)** and **(Thrust 2)**.

Thrust 4. Validation of our multi-scale modeling through simulations of ultrafast DDP experiments.

Currently, there are multiple theoretical models used to calculate thermophysical parameters and to simulate electron-ion nonequilibrium systems that are either condensed matter physics or plasma physics in origin. These approaches are largely deployable, however, there are significant discrepancies in their results between these models, and most importantly, a lack of systematic comparison between experiments and theoretical models. This has led to a confusing situation due to a lack of agreement between theory and experimental results over different systems and on different observables (such as optical absorption profile, onset slope of XANES, Debye Waller Factor) which are largely inconsistent[8]. As such, our initial focus will be to generate theoretical data over multiple systems and on multiple observables in a systematic manor so as to cross validate the extent of agreement over different observables and models. This will enable us to assess the limit of the models by quantifying the error and identifying the origin of the error, which in turn could be used to improve the models and/or develop enhanced alternative models. Our approach enables us to develop models without adjustable parameters, wherein observed discrepancy/agreement is a direct manifestation of the validity of, or lack thereof, the approximations. This in turn forces us to improve our theory to support baseline model development, rather than introducing new adjustable parameters.

In achieving our goals, we will fully leverage and integrate the software tools being developed at the DOE BES CMS Software Center for Non- Perturbative Studies Of Functional Materials Under Non-Equilibrium Conditions (NPNEQ), whose director is the PI of this initiative Tadashi Ogitsu. This will expand the capability of the RT-TDDFT code previously developed by co-PIs, Alfredo Correa and Xavier Andrade[9, 10], based on the scalable DFT code, Qbox, written by Francois Gygi[11]. One of the planned modifications of the code for NPNEQ will be a complete description of nonadiabatic and nonequilibrium electron-ion dynamics, which is necessary for achieving the overall goal of this initiative. However, the energy scales of interests are different: this initiative focuses on DDP problems, while NPNEQ focuses on condensed matter physics problems.

Another focus of NPNEQ is to optimize the RT-TDDFT code for current and future DOE Leadership Class High Performance Computer Systems at Oak Ridge, Argonne, NERSC and

LLNL. This initiative intends to exploit the full potential of both the software and the DOE HPC facilities.

Thrust 1: Improve Nonequilibrium Thermophysical Properties Within Perturbative/Adiabatic Approximations

In many cases, simulating experimentally created nonequilibrium DDP systems requires knowledge about electronic and ionic specific heats (C_e, C_i), electron-ion coupling ($G_{e\text{-}i}$), and electronic and ionic thermal conductivities (K_e, K_i), as input parameters of TTM simulations. The major issues in establishing these parameters are the lack of well-established methods that allow us to directly measure or computationally calculate accurate values for electron-ion nonequilibrium DDP conditions. It is for this reason, we propose to calculate these values based on known ab-initio methods described in Refs [8] and [12, 13], and/or the method based on the Fermi Golden rule for a series of metals that are suitable for experimental validations. The computational methods discussed in this white paper do not have adjustable parameters and the thermophysical parameters are linked uniquely through the electronic structure of the system at T_e, T_i. Therefore, observed discrepancy or agreement become clear measures of accuracy for approximations used in these methods. We will also use RT-TDDFT (described in **Thrust 2**) to investigate the origin of error (or lack thereof) for each approximation and, if necessary, develop and propose a revised approximation. Complete explanations as to how ab-initio parameter-free (G, C, K) can be found in Refs [8, 12-14].

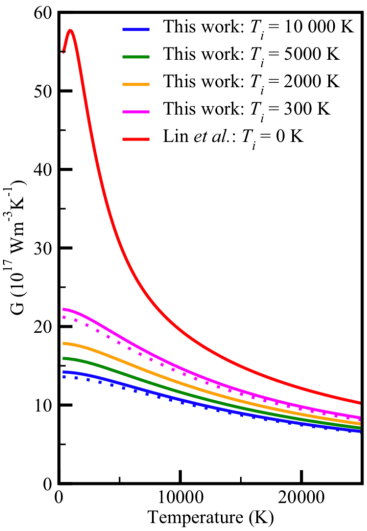

Figure 1: Electron-phonon coupling parameters calculated as a function of T_e at different T_i. The data of Lin *et al.* were calculated for a perfect bcc crystal at T = 0 K, while the rest are ensemble averaged values based on *ab initio* MD simulations. See Ref [8] for more details.

This Thrust will generate *G, C, K* of metals for broad ranges of T_e, T_i calculated with the candidate method described above, and the accuracy of methods will be assessed using the method described in **Thrust 4** using 1-TTM (**Thrust 3**). We will also extend the applicable physical conditions of these parameters to HEDP, wherein higher energy excitation is expected to alter the thermophysical parameters significantly.

Thrust 2: Expand Nonequilibrium Electron-Ion Coupling Derived From Non-Perturbative/Non-Adiabatic RT-TDDFT Simulations

In this thrust, we propose to expand the capability of our RT-TDDFT code developed under DOE BES CMS Software Center, NPNEQ. The software developed under NPNEQ focuses on condensed matter applications, while this initiative will implement specific algorithms and functionalities that are necessary for DDP research where the energy scale is large potentially requiring more advanced time integration algorithms. Below is a brief description of the underlying physics /algorithms of the RT-TDDFT method.

A *formally exact* approach to nonlinear and nonequilibrium dynamics under arbitrary time-dependent external fields is provided by the time-dependent DFT (TDDFT) and real-time (RT) formulation, which is *non-perturbative* in the external fields. Its applicability has already been demonstrated for modeling the explicit propagation of intense laser fields through solids[19]. For the time-dependent nonadiabatic electron-ion dynamics problem (See Fig. 2), quantum-classical[20], as well as fully quantum[21] approximations, have been proposed within the framework of TDDFT[22]. The former and latter approaches respectively treat the typically slower nuclear motions classically and quantum-mechanically, but always in conjunction with a quantum description of electrons. Among the quantum-classical approaches, the *Ehrenfest*[23] and *surface-hopping*[20] formulations have been explored in the molecular[20] and condensed phase[24], such as, nonadiabatic effects in electronic stopping power[25], electron-phonon coupling[26], polaron dynamics[24] and hot-electron dynamics[27]. A beyond-Ehrenfest dynamics that treat the ions semi-classically has been developed by Co-I **Correa.** This Effective Correlated Electron-Ion Dynamics (ECEID)[28] approach enables scalable time-domain nonequilibrium DDP applications. While Ehrenfest dynamics can be an accurate description of the evolution of the system for short times (fs), there is a systematic accumulation of errors producing a biased energy exchange, leading to electron-ion dynamics that does not lead to thermal equilibrium. ECEID, on the other hand, was shown to restore the correct limits for thermalization between nonequilibrium electronic and ionic degrees of freedom (see Fig. 3).

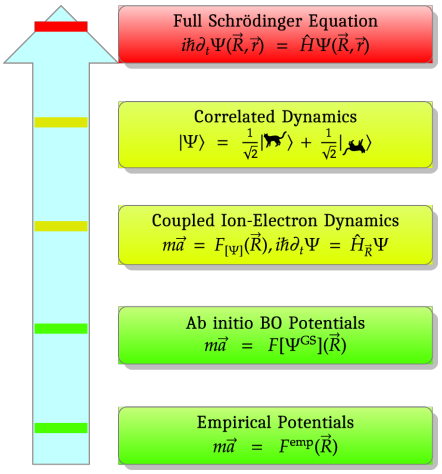

Figure 2: The molecular dynamics ladder of theories. The two lower boxes (green) indicate current practical methods. The top box (red) is the Holy Grail of atomistic dynamics. The two middle boxes (yellow) constitute the theories that will be developed under the NPNEQ center. The second yellow box is the approximated time-dependent theory that has correlation information and allows thermodynamic equilibration between the electronic quantum system and the quasi-classical ions.

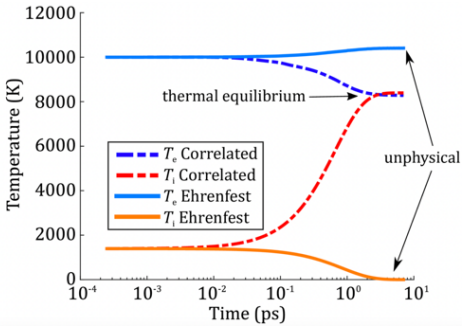

Figure 3: ECEID[28] approach correctly describes the thermalization process, while Ehrenfest dynamics fails.

The goals of **Thrust 2** are to expand the RT-TDDFT code for the DDP applications, and use it for assessment of $G_{e\text{-}i}$ parameters (**Thrust 1**), gain insights into electron-ion equilibration process of DDP systems (**Thrust 3-5**) and apply to the radiation damage process (**Thrust 6**).

Thrust 3: Develop Fully Electron-Ion Temperature Dependent 1D TTM

As it was shown in Ref [8], a direct comparison between theory and experimental results requires an ability to model the systems that are used in the experiments, which is generally too large for direct ab-initio simulations. In addition, it was shown that T_i dependence, in addition to T_e, is crucial in reproducing the experimental results. However, the 1D-TTM simulations were

performed without full T_e and T_i dependent *G, C, K* due to time and resource limitation. In order to perform a more reliable comparison with the experiments, it is highly desirable to use T_e, T_i dependent TTM simulations. To this end, we propose to expand our 1D-TTM code that could use only T_e dependent *G, C, K* in such a way that the new code can use fully T_e, T_i dependent *G, C, K*. This improved software will be utilized in **Thrust 4** using *G, C, K* developed in **Thrust 1**.

Thrust 4: Enhance Calculations of Observables for Validation and Experimental Design

Recently, constraining thermophysical properties under electron-ion non-equilibrium DDP conditions has been shown to be possible[8]. Detailed comparison with experiments indicated that both T_e and T_i dependence on parameters such as specific heat, electron-phonon coupling, and thermal conductivity may be important[8, 37-39]. In the recent study on warm dense iron[8, 39], these parameters were calculated based on ab-initio density functional theory (DFT) simulations, eliminating adjustable parameters. Using these, one can simulate the spatiotemporal evolution of electron and ion temperatures in thin metallic foils using TTM. Based on this, one can calculate the time evolution of spectroscopic profiles (XANES was used in this study) for a system triggered by a short pulse laser. By comparing the simulated time evolution of the XANES spectrum and the measured one, we showed that thermophysical parameters under electron-ion nonequilibrium DDP condition can be tightly constrained (see Fig. 5). If one performs XANES and Ultrafast Electron Diffraction (UED) experiments side-by-side on the same material, with similar geometry and laser fluence and pulse duration, we should be able to learn great deal about nonequilibrium DDP. XANES provides information about T_e and UED provides information about T_i as Debye Waller Factor (DWF). It was shown that for the onset slope of XANES, target thicknesses of about 2 to 8 times of the ballistic range of the conduction electrons will enable the thermal conductivity of iron to be constrained with accuracy less than a few tenths of a percent[8] (see Fig. 6).

The primary goal of this thrust is to provide data and software tools that allow researchers in the broader DDP/HEDP community to calculate the time evolution of theoretical spectroscopic

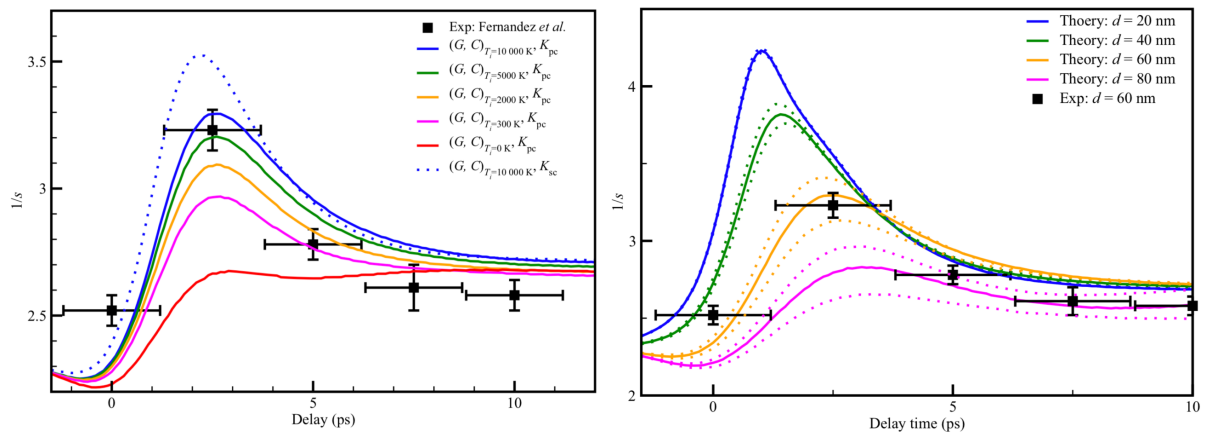

Figure 5 (left): Simulated *1/s* profiles for several sets of (*G, C, K*) parameters compared with the experimental values. **Figure 6 (right):** 1/s calculated with K_{PC} (solid lines) and with $K_{PC}\pm20\%$ (dashed lines) in order to show the *K* dependence of *1/s*. The pump laser fluences are chosen in such a way that the corresponding energy densities are equivalent to that of *d* = 60 nm (or value used in the experiments). *s* is the onset slope of XANES. K_{PC} is the calculated thermal conductivity of polycrystalline iron. Both from Ref [8]

profiles such as XANES, UED for a wide variety of materials and aid in the interpretation of their experimental results.

Programmatic Benefit

Currently, there is no reliable theoretical models that are capable of simulating nonequilibrium DDP. Together with theoreticians and experimentalist in the DDP/HEDP research community, our intention is to build computational platform that enables us to establish the reliable theoretical models that allow us to simulate DDP systems. Such models could be used in the community for robust interpretation of experimental results, which in turn, will facilitate the advancement of DDP/HEDP research fields.

US Leadership and Global Context

Understanding nonequilibrium DDP problems are relevant for advancing a variety of current and future technologies such as laser welding, additive manufacturing of metals, development of fast nuclear fission/fusion reactor materials. As such, success of our initiative will enhance US leadership in these fields. International collaborations that bring in the world leading experts will greatly accelerate the initiative's progress.

Timeline of the Initiative

Science and Technology Readiness: Our initiative proposes to develop novel methods and apply them with existing methodologies. Therefore, we are ready to immediately start the initiative activitiesy. Lack of funding support is only the barrier.

Community Preparedness (readiness for each thrust): Experimental validation (not a part of our proposal) related to **Thrust 4** requires specific experimental facilities such as UED and time resolved XAS beamline for DDP research. As far as we are aware of, the former exists at SLAC, LBNL. The preparedness for the latter will be a subject of debate at the workshop.

Equipment/Facility Design Details

No new equipment and/or facility is required.

Cost Range

The requested funding covers the level of FTEs needed for computational method development, conducting simulations, and analyzing the simulation results. This includes travel. We are requesting ~ $800k per year for 5 years. [3 x 0.30 FTE + 1 Post Doc Candidates]
For the experimental validations, we anticipate involvement from our current collaborators and advocates of our initiative listed below. Aaron Lindenberg of SLAC/Stanford, who is the co-PI of NPNEQ may also provide necessary experimental data.

Cross-Cutting Connections

This initiative addresses the cross-cutting area of Theory and Computation that will facilitate enhanced interpretation of various types of DDP/HEDP experiments.

Advocates of This Initiative

Roger Falcone (Univ. Berkeley), Phil Heimann (SLAC), Siegfried Glenzer (SLAC/Stanford), Felicie Albert (LLNL), Roald Redmer (Univ. Rostock), Shinsuke Fujioka (Osaka Univ.).

References

1. H. J. Lee, *et al.*, Phys. Rev. Lett. **102**, 115001 (2009).
2. J. Zhou, *et al.*, Phys. Rev. E **90**, 041102 (2014).
3. E. D. Murray *et al.*, Phys. Rev. B **75**, 184301 (2007).
4. V. Recoules *et al.,* Phys. Rev. Lett. **96**, 055503 (2006).
5. R. Ernstorfer *et al.*, Science **323**, 1033 (2009).
6. Z. Lin, L. V. Zhigilei and V. Celli, Phys. Rev. B **77**, 075133 (2008).
7. P. B. Allen, Phys. Rev. B **36**, 2920 (1987).
8. T. Ogitsu *et al.*, Phys. Rev. B **97** (21), 214203 (2018).
9. A. Schleife, E. W. Draeger, Y. Kanai and A. A. Correa, J. Chem. Phys. **137**, 22A546 (2012).
10. E. W. Draeger *et al.*, J. Para. Dist. Comp. **106**, 205 (2017).
11. F. Gygi, IBM J. Res. Dev. **52**, 137 (2008).
12. J. Simoni and J. Daligault, Phys. Rev. Lett. **122**, 205001 (2019).
13. J. Daligault and J. Simoni, arXiv preprint arXiv:1906.01610 (2019).
14. L. Waldecker, R. Bertoni, R. Ernstorfer and J. Vorberger, Phys. Rev. X **6**, 021003 (2016).
15. G. V. Chester and A. Thellung, Proc. Phys. Soc. **77**, 1005 (1961).
16. L. Onsager, Phys. Rev. **37**, 405 (1931).
17. X. Y. Wang, D. M. Riffe, Y. S. Lee and M. C. Downer, Phys. Rev. B **50**, 8016 (1994).
18. P. B. Allen, Phys. Rev. Lett. **59** (13), 1460-1463 (1987).
19. K. Yabana, T. Sugiyama, Y. Shinohara, T. Otobe and G. F. Bertsch, Phys. Rev. B **85**, 045134 (2012).
20. F. Agostini, B. F. E. Curchod, R. Vuilleumier, I. Tavernelli and E. K. U. Gross, in *Handbook of Materials Modeling : Methods: Theory and Modeling*, edited by W. Andreoni and S. Yip (Springer International Publishing, Cham, 2018), pp. 1-47.
21. Y. Yang, T. Culpitt and S. Hammes-Schiffer, J. Phys. Chem. Lett. **9**, 1765 (2018).
22. M. A. Marques, N. T. Maitra, F. M. Nogueira, E. K. Gross and A. Rubio, *Fundamentals of time-dependent density functional theory*. (Springer Science & Business Media, 2012).
23. I. Tavernelli, U. F. Röhrig and U. Rothlisberger, Mol. Phys. **103**, 963 (2005).
24. G. Kolesov, O. Grånäs, R. Hoyt, D. Vinichenko and E. Kaxiras, J. Chem. Theo. Comp. **12**, 466 (2016).
25. A. Schleife, Y. Kanai and A. A. Correa, Phys. Rev. B **91** (1), 014306 (2015).
26. A. Tamm *et al.*, Phys. Rev. B **94**, 024305 (2016).
27. L. Li and Y. Kanai, Phys. Chem. Chem. Phys. **20**, 12986 (2018).
28. V. Rizzi, T. N. Todorov, J. J. Kohanoff and A. A. Correa, Phys. Rev. B **93**, 024306 (2016).
29. A. Gómez Pueyo, M. A. L. Marques, A. Rubio and A. Castro, J. Chem. Theo. Comp. **14**, 3040 (2018).
30. Z. Wang, S.-S. Li and L.-W. Wang, Phys. Rev. Lett. **114**, 063004 (2015).
31. Y. Zhu and J. M. Herbert, J. Chem. Phys. **148**, 044117 (2018).
32. W. Jia, D. An, L.-W. Wang and L. Lin, J. Chem. Theo. Comp. **14**, 5645 (2018).
33. D. Duffy and A. Rutherford, J. Phys.: Cond. Matt. **19**, 016207 (2006).
34. A. Tamm *et al.*, Phys. Rev. Lett. **120**, 185501 (2018).
35. T. Chase, *et al.*, App. Phys. Lett. **108**, 041909 (2016).
36. P. Maldonado *et al.*, arXiv preprint arXiv:1906.08504 (2019).

37. B. I. Cho *et al.*, Phys. Rev. Lett. **106**, 167601 (2011).
38. B. I. Cho *et al.*, Sci. Rep. **6**, 18843 (2016).
39. A. Fernandez-Panella *et al.*, submitted (2019).
40. P. Sigmund, Nuc. Inst. Meth. Phys. Res. Sec. B **85**, 541-550 (1994).
41. A. Akkerman, A. Breskin, R. Chechik and Y. Lifshitz, Radi. Phys. Chem. **61**, 333 (2001).
42. D. Emfietzoglou, M. Moscovitch and A. Pathak, Nuc. Inst. Meth. Phys. Res. Sec. B **212**, 101 (2003).
43. D. Emfietzoglou *et al.*, Nuc. Inst. Meth. Phys. Res. Sec. B **242**, 55 (2006).
44. Z. Tan, Y. Xia, M. Zhao and X. Liu, Nuc. Inst. Meth. Phys. Res. Sec. B **248**, 1 (2006).
45. R. Garcia-Molina *et al.*, Nuc. Inst. Meth. Phys. Res. Sec. B **267**, 2647 (2009).
46. K. Nordlund, Comp. Mater. Sci. **3**, 448 (1995).
47. G. Collaboration and S. Agostinelli, Nucl. Instrum. Meth. A **506**, 0 (2003).
48. G. Battistoni *et al.*, Frontiers in oncology **6**, 116 (2016).
49. J. F. Ziegler, M. D. Ziegler and J. P. Biersack, Nuc. Inst. Meth. Phys. Res. Sec. B **268**, 1818 (2010).
50. E. E. Quashie, B. C. Saha and A. A. Correa, Phys. Rev. B **94**, 155403 (2016).
51. E. E. Quashie and A. A. Correa, Phys. Rev. B **98**, 235122 (2018).
52. E. E. Quashie, B. C. Saha, X. Andrade and A. A. Correa, Phys. Rev. A **95**, 042517 (2017).

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344.